Voltammetric determination of caffeine by using gold nanoparticle-glassy carbon paste composite electrode

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ABSTRACT

In the present study, simple and sensitive voltammetric determination of caffeine was carried out by using a gold nanoparticle-glassy carbon paste composite electrode (AuNP-GCPE) in 3.2 mM H_2SO_4 (pH 2.5). The effects of supporting electrolyte, pH and AuNP amount on caffeine peak current were investigated. After the optimization of experimental parameters, analytical characteristics of AuNP-GCPE were examined and two linear ranges were obtained between 25–150 μM and 200–1000 μM with limit of detection values of 0.96 μM and 4.90 μM, respectively. Relative standard deviation for 50 μM caffeine was also calculated as 7.52% ($n = 3$). In order to evaluate the analytical performance of AuNP-GCPE, caffeine contents of various brands of cola samples were measured and compared with the results obtained by UV–Vis spectrometer. The obtained results by using the proposed composite electrode are in accordance with the caffeine contents that manufacturers claimed compared to UV–Vis. This composite electrode which utilizes the catalytic effect of AuNP with the simple preparation of GCPE, offers a fast and sensitive determination of caffeine in beverages as a practical application.

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1. Introduction

Caffeine, a methylxanthine derivative, is a natural alkaloid which is the main component of daily consumed beverages and food like coffee, tea, coke, energetic drinks and chocolate [1,2]. Besides, caffeine is also used in several pharmaceutical formulations due to its psychoactive effects such as stimulation of central nervous system, diuresis and gastric acid secretion [1,3]. On the other hand, excessive intake of caffeine may cause mutagenic effects in DNA repair. This situation also affects cyclic AMP phosphodiesterase activity and causes cardiovascular problems, kidney diseases and complications in pregnancy [2,4,5]. Furthermore, caffeine intake in doses of 150–200 mg kg^{-1} of body weight is considered to be fatal [2]. Thus, the development of a fast and sensitive method for caffeine determination is vital for testing food quality and for clinical applications.

Numerous analytical methods have been developed for the caffeine determination up to now. Most of these methods are based on spectroscopic [6–8] and hyphenated chromatographic techniques [9–11] in which remarkable results were obtained in terms of sensitivity. However, these methods are complicated, laborious and time consuming which need sample pre-treatment procedures

and expensive bulky equipments [2]. As an alternative choice, electrochemical methods have attracted a considerable attention by providing fast and sensitive caffeine detection in a wide variety of samples with simple and low cost instrumentation [2,4,5,12–18]. Moreover, in most cases there is no need to use sophisticated sample pre-treatment procedures prior to analysis. However, electrochemical methods suffer from more positive oxidation potential of caffeine which leads to large background currents in blank solution and strongly adsorbed oxidation products on the electrode surface [13].

In order to overcome these limitations, carbon based composite electrodes may provide an opportunity for the electrochemical determination of caffeine by combining the superior properties of the materials used in the electrode fabrication. Also, since these electrodes are practical in terms of renewal and preparation procedures, they can solve problems. Besides these, composite electrodes may be adapted to various electrode configurations with great flexibility in size and shape of the material [19]. Glassy carbon paste electrode (GCPE) is a kind of composite carbon electrode which can be easily prepared just by mixing proper amount of glassy carbon microparticles and oil binder. GCPE can be defined as a favourable candidate among carbon based electrodes due to its higher electrochemical reactivity, wider potential window and low background current as well as its easy preparation at low cost. Also, since it is easy to renew the surfaces of these electrodes, fresh

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surfaces are obtained prior to each measurement which make their usages advantageous in the case of strongly adsorbed oxidation products. Since the components used in electrode fabrication are homogeneously dispersed and compressed in the bulk of the structure, it is possible to obtain reproducible results with every new surface [19–21]. To the best of our knowledge, although there are several research papers based on the usage of carbon based electrode itself and also as the component of the composite electrode fabrication for caffeine detection, GCPE has not been used for this purpose [22–26].

To date, several researches dealing with GCPE have been performed and nanomaterials and biomolecules were used to improve the electronic and catalytic properties of these composite electrodes [19,21,27]. Among these materials, owing to its higher conductivity, larger surface area and applicability in biosensing platforms, gold nanoparticles (AuNP) became very popular and were also utilized for the electrode modification in voltammetric determination of caffeine [28,29]. By taking into consideration of these unique properties of GCPE and AuNP, these mentioned features may be combined to bring new insights into the composite electrode fabrication especially for caffeine detection.

Thus, in the present study, it was aimed to fabricate a composite electrode by combining the properties of AuNP and GCPE for the rapid and sensitive voltammetric determination of caffeine for the first time. After the optimization of the experimental conditions and the examination of analytical characteristics, AuNP-GCPE was applied to the determination of caffeine amount in various cola beverage samples and the results were compared with UV–Vis spectroscopy.

2. Experimental

2.1. Apparatus

Differential pulse voltammetry (DPV) measurements were carried out with AUTOLAB PGSTAT 12 electrochemical measurement system (ECO CHEMIE Instruments B.V., The Netherlands) equipped with NOVA 1.10 software. The experiments were conducted in a 10 mL voltammetric cell using conventional three-electrode configuration consisted of GCPE or AuNP-GCPE as the working electrode, Ag/AgCl and platinum wire as the reference and the counter electrodes, respectively. Absorbance measurements were performed on a T60 model UV–Vis spectrometer (PG Instruments, England).

2.2. Reagents and materials

All reagents were used as received without further purification. Caffeine was purchased from Merck. Glassy carbon spherical powder (2–12 μm, 99.95% metals basis), mineral oil and gold colloid (0.75 A520 units/mL; 10 nm ∼0.001% as $HAuCl_4$) were obtained from Sigma-Aldrich for the preparation of GCPE and AuNP-GCPE. 3.2 mM H_2SO_4 (pH 2.5) was used as the supporting electrolyte. pH of the supporting electrolyte was adjusted with 0.1 M KOH (Riedel-de Haën). All solutions were prepared with double distilled water.

2.3. Preparation of AuNP-GCPE

AuNP-GCPE was prepared in the composition of 80:20 (w/w%) glassy carbon paste powder/mineral oil with 1 μL of gold colloid by hand-mixing. The required amount of the homogeneous paste was filled into the electrode cavity of a Delrin tube where electrical contact was provided via a copper wire. The surface was smoothed

on a weighing paper and rinsed with double distilled water prior to measurement.

2.4. Procedure

The oxidation peak of caffeine was obtained by scanning potential from 0.8 V to 1.6 V in differential pulse mode with a 0.005 V of step potential, 0.025 V of modulation amplitude and scan rate of 10 mV/s using 3.2 mM H_2SO_4 (pH 2.5) as the supporting electrolyte. Prior to each measurement, AuNP-GCPE surface was renewed and the reference electrode was rinsed with double distilled water. Pt wire was sonicated for 3 min in 0.1 M H_2SO_4 to remove strongly adsorbed oxidation products of caffeine.

2.5. Sample preparation

Different branded cola samples were purchased from a local supermarket and stored at room temperature until sample preparation. Cola samples were degassed by ultrasonication for 10 min and diluted in the ratio of 1:10 (v/v) with supporting electrolyte containing a known amount of caffeine standard solution [4].

3. Results and discussion

The optimization studies including pH effect and AuNP amount were conducted in the first place. For optimum pH study, plain GCPE was used. Then, optimization of AuNP amount was found. After that, analytical characteristics and sample application were made.

3.1. Influence of pH

The influence of pH on caffeine oxidation peak current was evaluated in presence of 50 μM caffeine by varying pH from 1.0 to 6.0. Within this scope, pH dependence of caffeine peak current was examined using GCPE in pH ranges 1.0 to 3.0 with H_2SO_4 solution, 3.0 to 5.0 with acetate buffer and at pH 6.0 with phosphate buffer, respectively. As shown in Fig 1, the highest peak current was obtained for pH 2.5 in case of using 3.2 mM H_2SO_4 at GCPE. Since the highest peak current at GCPE was obtained in pH 2.5, further experiments using AuNP-GCPE were also conducted at the same pH.

3.2. Effect of AuNP amount

The amount of AuNP was varied as 0.5, 1, 2, 5 and 10 μL to examine the relationship between AuNP amount and peak current of 50 μM caffeine. As depicted in Fig 2, peak current increased up
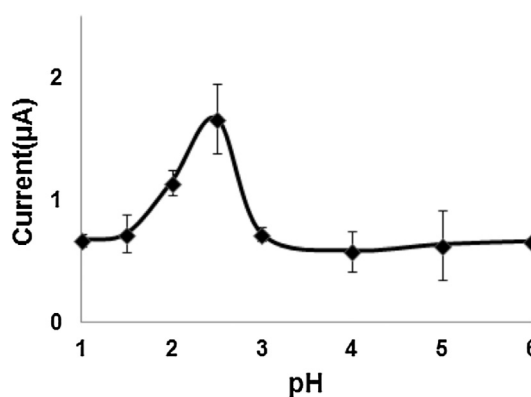

Fig. 1. The influence of pH on voltammetric response of 50 μM caffeine using GCPE.